# TO BURN OR NOT TO BURN – HIGH OXYGEN MIXTURES

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## Oxygen Combustion

The use of enriched oxygen breathing mixtures in recreational and technical diving is on the increase, and reports about oxygen combustion and explosions are documented. It is also commonly known that flammable materials are more easily ignited as oxygen concentration increases. It is also well known that many systems in the diving industry were designed for high pressure air flows (oxygen percentage below 21%), and that accidents have occured in such systems with higher concentrations of oxygen. In the recreational realm, concerns thus surface for nitrox diving, while in the technical realm, concerns center on all enriched mixtures of nitrogen and helium, plus the use of pure oxygen for decompression.

Before launching off into a detailed analysis of oxygen combustion, explosions, and related risks, some observations on enriched oxygen diving and equipment are interesting:

1. the safety record for nitrox diving with recreational scuba equipment is excellent, literally millions of dives without mishap;
2. the safety record for technical diving on enriched breathing mixtures, plus pure oxygen, is even more impressive than the recreational record;
3. when nitrox was introduced to recreational diving, it was greeted with much skepticism;
4. enriched oxygen breathing mixtures and pure oxygen in the technical diving community has always been business as usual;
5. nitrox, helitrox, and pure oxygen usage are advanced diver topics, and require special training and education;
6. recommended training measures in mixed gas courses include verification that the equipment is suitable to exposures with high oxygen content, cleaning to remove combustible contaminants such as lint, oil residue, flammable dirt, and metal chips, and substitution of components and lubricants with oxygen compatible materials;
7. across the board, training agencies permit interchangeable use of equipment for air and nitrox diving when oxygen fractions are below 40%;
8. oxygen cleaning requirements for the USN and OSHA are also in effect for mixtures with more than 40% oxygen.

Oxygen doesn't burn itself, obviously, but chemical oxidation (by $O_2$) is what causes fires and explosions. The higher the oxygen concentration, the higher will be material flammability and explosive risk. Many studies have established that common substances that do not burn in air will burn at higher pressures and oxygen concentrations. Included in this category are neoprene, silicone rubber, nitrile rubber, and nylon. Though the frequency of fires in systems with less than 40% oxygen is less than than those with 100% oxygen, incidents in the former case have been recorded in aluminum and carbon steel compressor blocks, aluminum filter towers, fill station panel valves and regulators, and continuous blending systems.

**Bench Tests**

Within the diving industry, systems with oxygen concentrations greater than 41% are treated as 100% oxygen regarding cleaning and oxygen service. Systems with 21% to 26% oxygen require no special cleaning. Between 40% and 25%, opinions and procedures vary widely. Most know that fires occur in 100% oxygen systems, but less known are fires in 46% oxygen systems, such as NASA's Neutral Buoyancy Laboratory (NBL). So a big question centers around the 25% to 40% oxygen concentrations and potential combustion risk. Many materials that are not flammable in air are flammable in 25% to 40% nitrox environments, as seen in Table 1 compiled by Forsyth and Durkin. Though the frequency of nitrox fires with oxygen fractions below 40% is far less than 100% pure oxygen, many have been reported. The most common occurrence is fill stations. Hyperbaric chambers are other sites experiencing fires at higher oxygen pressures, $ppO_2$s.

From Table 1, PEEK, neoprene, PVC, silicon rubber, nitrile rubber, nylon, and EPDM may not support combustion in ambient air, but likely would in 40% oxygen mixtures. As pressure, $P$, increases up to a point, oxygen index (OI) generally decreases, so that some typical scuba materials like PTFE and PCTFE may become flammable. Fire hazards are real, even in systems with lower oxygen concentrations than 40%.

Table 1. Material Flammability And Oxygen Index (Fraction)

| material | oxygen index (%) |
|---|---|
| EPR | 21 |
| EPDM | 20 - 25 |
| nylon | 21 - 38 |
| nitrile rubber | 22 |
| silicone rubber | 25 - 39 |
| PVC | 31 |
| neoprene | 32 - 35 |
| PEEK | 35 |
| vespel | 53 - 61 |
| viton FKM | 56 |
| kel PCTFE | 95 - 100 |
| teflon PTFE | 95 - 100 |

Both contaminant ignition and pneumatic impact bench studies have been conducted in scuba assemblies and breathing gas delivery systems by NASA for 50% and 100% oxygen systems. No ignitions occured during impact tests, though assembles contained gross amounts of particulates and hydrocarbons. Ignition studies were conducted in stainless steel tubes contaminated with hydrocarbon oil. Upon pneumatic impact, ignitions were observed in both 50% and 100% oxygen mixtures for concentrations as low as 10 $mg/ft^2$, and drive pressures as low as 1000 $psi$. No ignitions were observed at drive pressures below 500 $psi$.

**Ignition And Propagation Simulations**

The question of oxygen combustion in high pressure flows is important in mixed gas diving. Reports of cylinder and regulator explosions with enriched and pure oxygen breathing mixtures abound. Using sophisticated 3D hydrodynamics codes with oxygen combustion chemistry embedded, it is also possible to quantify some explosion scenarios under high pressure pneumatic impacts of combustible particles (dirt). Mixed gas flows (variable oxygen fraction) down a short stopped tube can be analysed for variable volatile and nonvolatile particle densities in an impact region (stopped end with a small opening simulating the first stage seat of a regulator). Drive pressures were varied from 50 $psi$ to 5000 $psi$, with dirt particle densities ranging from 5 $mg/ft^2$ up to 300 $mg/ft^2$, and oxygen fractions from 0.21 up 1.00 (air to pure oxygen). Some results are given in Tables 2 - 4, with

$X$ underscoring ignition and burn, and $O$ denoting no ignition and burn. The KIVA code of Amsden and Ramshaw was employed for numerical simulations, using the previous combustion equations.

Flow schemes are typical of impacted pneumatic gas hydrodynamics. At the stopped orifice, a slug of compressed gas is heated by both shock formation and inertial implosions (compressive and non-adiabatic). Dust is assumed to be metal, plastic, glass, grit, rubber, and fiber, with particle sizes ranging 5 $\mu m$ to 250 $\mu m$. Plastic, fiber, rubber, and hydrocarbons are combustive. Reaction oxygen chemistry is assigned to the dust, and rapid heat conduction from the slug ignites assembly constituents. Certainly, the burn process is very complicated, but some simple results are suggested by these numerical simulations as seen in Tables 5 - 7.

Table 2. Drive Pressure 1000 *psi*

| dirt<br>($mg/ft^2$) | oxygen (%)<br>20 | oxygen (%)<br>40 | oxygen (%)<br>60 | oxygen (%)<br>80 | oxygen (%)<br>100 |
|---|---|---|---|---|---|
| 50 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 100 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 150 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 200 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 250 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 300 | $O$ | $O$ | $O$ | $O$ | $X$ |

Table 3. Drive Pressure 3000 *psi*

| dirt<br>($mg/ft^2$) | oxygen (%)<br>20 | oxygen (%)<br>40 | oxygen (%)<br>60 | oxygen (%)<br>80 | oxygen (%)<br>100 |
|---|---|---|---|---|---|
| 50 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 100 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 150 | $O$ | $O$ | $O$ | $O$ | $O$ |
| 200 | $O$ | $O$ | $O$ | $X$ | $X$ |
| 250 | $O$ | $O$ | $O$ | $X$ | $X$ |
| 300 | $O$ | $O$ | $X$ | $X$ | $X$ |

Table 4. Drive Pressure 5000 *psi*

| dirt<br>($mg/ft^2$) | oxygen (%)<br>20 | oxygen (%)<br>40 | oxygen (%)<br>60 | oxygen (%)<br>80 | oxygen (%)<br>100 |
|---|---|---|---|---|---|
| 50 | $O$ | $O$ | $O$ | $O$ | $X$ |
| 100 | $O$ | $O$ | $O$ | $O$ | $X$ |
| 150 | $O$ | $O$ | $O$ | $X$ | $X$ |
| 200 | $O$ | $O$ | $O$ | $X$ | $X$ |
| 250 | $O$ | $O$ | $O$ | $X$ | $X$ |
| 300 | $O$ | $O$ | $X$ | $X$ | $X$ |

For drive pressures in the 3000 *psi* and above range, and across all dust densities supporting combustion, oxygen mixtures below 70% (oxygen fraction) did not ignite in these simple simulations. Above 70%, impurity densities around 200 $mg/ft^2$ were requisite to support combustion in the 3000 *psi* range. Below 3000 *psi*, ignition and burn were only sustained with high oxygen fraction (90% or so).

These are ignition studies. Deflagration and sustained burn are not guaranteed following ignition. In cases above, sustained burn requires rich oxygen mixtures, somewhere in the 70% range, and for dirt densities above 200 $mg/ft^2$. In the above, ignition and sustained burn produced 90% combustion of particulate matter. Only hydrocarbons (plastic, silicone, nylon) ignited in the simulations. Glass, titanium, and aluminum did not ignite. Two component mixtures, with hydrocarbon particulate density above 200 $mg/ft^2$ ignited, but the quenching component of the distribution (metal, glass) reduced the burn wave intensity. Below 5 $mg/ft^2$ dirt density, ignition and burn were not observed.

What does all this add up it to?

The suggestion is that, in both recreational and technical diving communities, combustion of enriched oxygen mixtures during diving does not occur, and statistics suppport the same. During filling, pure oxygen is to be treated carefully, with combustive risk increasing with oxygen percentage, but spontaneous explosions are also highly unlikely below 5,000 *psi* drive pressures. The early, highly emotional, fervor against enriched oxygen diving (nitrox, helitrox, pure oxygen in the shallow zone, etc) has subsided today. Thanks, divers, for being party to this.

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